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Short communication

Vanadium oxide electrode synthesized by electroless deposition for electrochemical capacitors

Haoran Wu, Keryn Lian*

Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3E4, Canada

HIGHLIGHTS

- A hydrous vanadium oxide was produced by simple electroless deposition.
- The deposited vanadium oxide is porous and contains a mixture of V^{5+} and V^{4+}.
- The chemical deposited electrodes are promising for electrochemical capacitors.

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ABSTRACT

A thin film vanadium oxide electrode was synthesized by a simple electroless deposition method. Surface and structural analyses revealed that the deposited oxide is a mixture of amorphous V_2O_5 and VO_2. Electrochemical characterizations of the synthesized vanadium oxide showed capacitive behavior with good cycle life. The electroless deposition of vanadium oxide is inexpensive, easy to process, and environmentally benign, offering a promising route for electrode development for electrochemical capacitors.

1. Introduction

Vanadium oxides, especially V_2O_5, VO_2, and $H_2V_3O_8$, have been investigated as electrodes for electrochemical capacitors (EC) due to their low cost, abundance, and their potential pseudocapacitive characteristics [1–9]. They are promising pseudocapacitive electrode materials, but their electrochemical performance depends strongly on their structure, chemistry, and morphology [1,3,5], which often result from the methods of synthesis.

As electrodes for ECs, vanadium oxides have been produced via sol–gel formation [2], hydrothermal synthesis [3], atomic layer deposition [4] and electrodeposition [5–9]. The electrodes synthesized by these methods exhibited a large variation in electrochemical behavior. For example, V_2O_5 prepared as a sol–gel [2] showed a capacitance of 1300 Fg^{-1} at a slow rate of 0.1 mVs^{-1}. In this form, vanadium oxide is a good bulk material for energy storage but is less suitable for high rate applications. $H_2V_3O_8$ synthesized by a hydrothermal process showed a specific capacitance of 121 Fg^{-1} or 236 $mFcm^{-2}$, but with a non-ideal cyclic voltammogram [3]. Mixed oxide VO_x (VO_2, V_2O_3, and V_2O_5) produced by atomic layer deposition [4] exhibited a capacitance of 600 Fg^{-1} and high power capability at 1 Vs^{-1}. Nonetheless, scale-up may involve significant capital costs. Electrodeposition [5–9] is an attractive low-cost method of producing vanadium electrodes but considering energy input and setup requirements, alternative methods that further simplify the production process would be even more appealing. Electroless deposition might be the simplest route, but so far, there are no reports on leveraging this method to synthesize vanadium oxides based electrodes for ECs. In this paper we present an inexpensive and easy-to-process electroless deposition method to produce vanadium oxide electrodes with electrochemical behavior suitable for EC applications.

2. Experimental

The substrate for vanadium oxide deposition was a thin titanium foil (0.13 mm, McMaster-Carr), ultrasonically cleaned for 5 min each in acetone, methanol, and DI water. Each Ti substrate was submerged in $VOSO_4$ solutions in the selected concentration. 0.3 ml of 1 M NaOH was added into each 25 ml plating solution to initiate

* Corresponding author.
E-mail address: keryn.lian@utoronto.ca (K. Lian).

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the precipitation process. The Ti substrate was kept in this solution under ambient conditions until the substrate was covered by a greenish film.

The effects of $VOSO_4$ concentration and deposition time on the capacitance of the electrode were studied. Deposition baths were prepared with $VOSO_4$ concentrations of 0.25M, 0.5M, and 0.75M. Three samples of Ti substrates where submerged into each bath. A coated sample was removed from the solution and measured at the same time on day 3, 5, and 7, respectively. The experiment was repeated 3 times. All three electrodes showed similar CVs (shown in Fig. S1) with a variation in capacitance below 7%. In the following, the electrodes are referred to by their experimental conditions, e.g., “0.5M–5days” for the electrode plated in 0.5M $VOSO_4$ for 5 days.

The surface morphology of the electrodes was examined by an FEI Quanta FEG 250 environmental scanning electron microscope (ESEM). X-ray diffraction (XRD) analyses were conducted using a Philips XRD system with a monochromatized CuKα anode. The surface chemistry of the electrodes was analyzed with X-ray photoelectron spectroscopy (XPS) using a thermo scientific K-Alpha instrument.

The electrochemical properties of the electrodes were characterized in a 1 M LiCl electrolyte via cyclic voltammetry (CV) utilizing an Ivium CompactStat in a 3-electrode beaker cell. Ag/AgCl was used as the reference electrode and a large Ti foil was used as the counter electrode. The area-specific capacitance was calculated by integrating the charge stored in the cathodic scan and divided by the voltage window and apparent area. In addition, a symmetric two-electrode EC cell was assembled from the vanadium oxide electrodes. The two electrodes were separated with a 0.17 mm thin filter paper soaked in 1 M LiCl solution. CV tests were conducted at a scan rate of 5 mVs^{-1}.

3. Results and discussion

The appearance and the capacitance of the electrolessly deposited vanadium oxides were found closely related to the concentration of $VOSO_4$ and the deposition time. After 3 days of deposition, a greenish coating appeared on the Ti substrates. From day 3 to day 5, the coating became visibly thicker, especially in the 0.25M and 0.5M solutions. However, inhomogeneities and island-like structures were observed after further soaking; in the 0.75M $VOSO_4$ solution the coating thickness even appeared to decrease. The area-specific capacitance of the samples (measured by CV) as a function of deposition time is shown in Fig. 1(a). A significant increase in specific capacitance can be observed from day 3 to day 5, with the capacitance approaching a plateau after day 5. Based on visual inspection of coating coverage (Fig. S2) and the measured capacitance in Fig. 1, 5 days of electroless deposition appeared to be the best condition, and thus the following discussion is based on the 5-day samples.

The CVs of the vanadium oxide electrodes (after 5-day deposition in 0.25M, 0.5M, and 0.75M $VOSO_4$ plating solutions) in 1 M LiCl electrolyte are shown in Fig. 1(b). The CV of a bare Ti substrate is overlaid as baseline. The Ti substrate shows a small capacitance of 0.03 mF cm^{-2}. In contrast, the vanadium oxide electrodes show much higher area-specific capacitance of 60.3 mF cm^{-2}, 67 $mFcm^{-2}$, and 41.9 $mFcm^{-2}$ for the 0.25M–5days, 0.5M–5days, and 0.75M–5days electrodes, respectively. Although the 0.25M–5days electrode shows a high capacitance, its CV profile is distorted when compared to the 0.5M–5days electrode which exhibits an ideal rectangular CV in the voltage window from 0 V to 0.6 V. The 0.75M–5days electrode also shows good CV behavior, but its capacitance is lower.

Fig. 2 shows the surface morphologies of the vanadium oxide electrodes produced by 5-day deposition at the three concentrations. All electrodes exhibit a highly porous surface of mixed meso- and macro-pores, similar as reported by Hu et al. using electrodeposition [6–8]. Figs. 2(a)–(c) show the SEM top view of the 0.25M–5days, 0.5M–5days, and 0.75M–5days electrodes. Judging from the surface morphologies observed in SEM, the 0.5M–5days electrode has the finest microstructure and porosity, see Fig. 2(b), which corresponds to a high area-specific capacitance. The side views of these electrodes are provided in Fig. 2(d)–(f): All electrodes show a dense layer interfacing between the Ti substrate and the porous vanadium oxide layers. The 0.5M–5days electrode has the highest coverage and the most intimate contact between the porous layer and the compact layer. In contrast, the 0.25M–5days electrode in Fig. 2(d) shows a much looser adherence between the coating and the Ti substrate, and Fig. 2(f) reveals low oxide coverage of the 0.75M–5days electrode. These observations support the results in Fig. 1 and suggest that 5-day deposition in 0.5M $VOSO_4$ (0.5M–5days) yields the best morphology to achieve high capacitance.

The surface composition of the electrodes was obtained by XPS analyses. Since the binding energies of V2p and O1s are very close, the high resolution spectra of V and O for the 0.5M–5days electrode are shown together in Fig. 3(a). The $V2p3_{/2}$ spectrum shows two oxidation states with binding energies at 515.9 eV for V^{4+} and 517.4 eV for V^{5+} [10–12]. The O1s spectrum was deconvoluted into 3 peaks at 531.7 eV, 530.4 eV and 529.8 eV, which correspond to H–O–H, V–OH, and V–O–V, respectively [6,11]. Based on the V2p

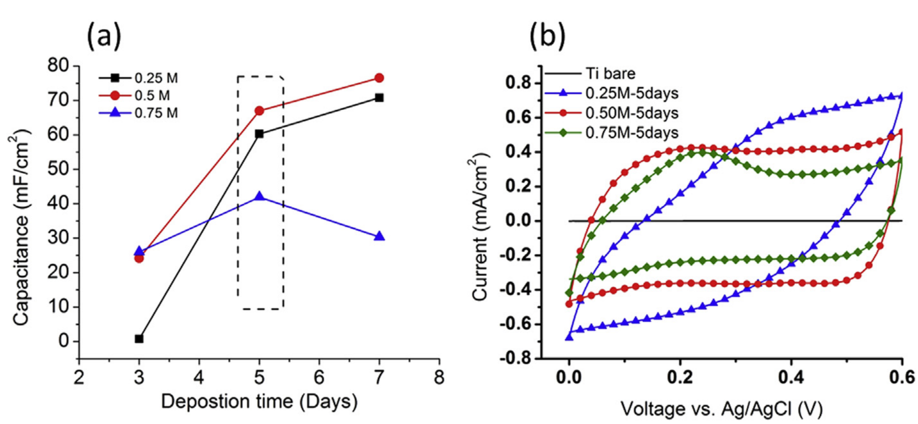

Fig. 1. (a) Capacitance vs. deposition time in 0.25M, 0.5M, and 0.75M $VOSO_4$ baths for vanadium oxide electrodes, measured at 5 mVs^{-1}; (b) CVs of 0.25M–5days, 0.5M–5days, 0.75M–5days, and Ti electrodes in 1 M LiCl at 5 mVs^{-1}.

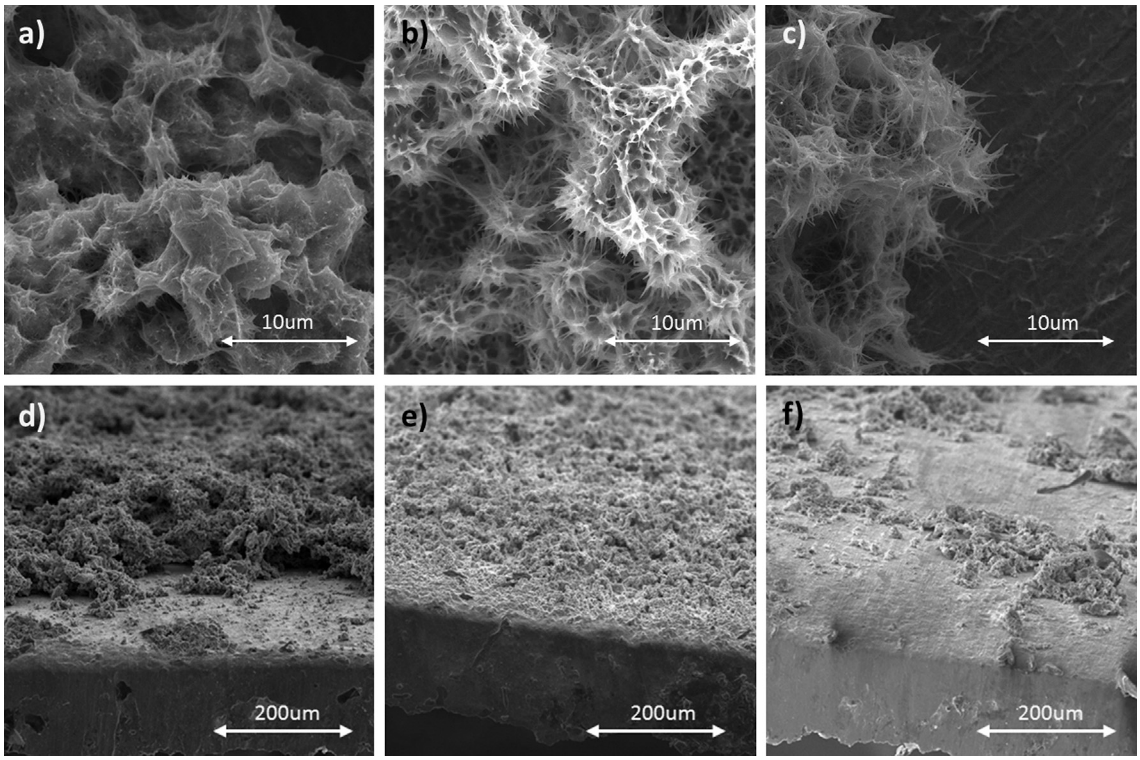

Fig. 2. Surface morphologies of the electrodes in Fig. 1(b); (a)–(c) top view and (d)–(f) side view of 0.25M–5days, 0.5M–5days, and 0.75M–5days electrodes.

and O1s spectra, the electrode material is likely mixed hydrous V_2O_5 and VO_2 similar to the materials obtained from electrodeposition by Hu et al., who suggested the composition to be $VO_x{\cdot}yH_2O$ [6–8]. Based on experimental observations and XPS analyses, Minch et al. proposed that the VO^{2+} ions reacted with OH^- to precipitate $VO(OH)_2$ according to the reaction shown in Equation (1) [13]:

$$2NaOH + VOSO_4 \rightarrow VO(OH)_2 + Na_2SO_4 \quad (1)$$

The precipitations initially dispersed in the solution and subsequently condensed on the Ti substrate. Since the solution and the specimen were exposed to air, the deposited V(IV) was partially oxidized to V(V) as observed in the XPS spectra. In Hu's work, a V^{5+} content of 89 mol% was reported, which is comparable to the V^{5+} concentration of 83 mol% observed in this work.

Based on the XRD pattern in Fig. 3(b), the structure of the deposited vanadium oxide (0.5M–5days) appears to be amorphous, likely due to the high level of hydration. It was suggested that amorphous and nanocrystalline V_2O_5 exhibit pseudocapacitive behavior [1], which is also the case for the electrolessly deposited vanadium oxides in this work. Comparing the CV profile in Fig. 1(b) with those of crystalline VO_2 and V_2O_5 reported in the literature [14,15], the amorphous vanadium oxide from electroless deposition exhibits a much more rectangular shape and thus is a better electrode material for ECs than crystalline VO_2 and V_2O_5.

In order to test its cycle life, the 0.5M–5days electrode was subjected to 3000 CV cycles in 1 M LiCl solution, as shown in Fig. 4(a). Vanadium oxide had been reported to have poor structural stability during charging–discharging due to material pulverization and dissolution in the electrolyte [3,16,17]. Instead of the severe degradation reported, our electrode showed only around 10% decrease in capacitance over 3000 cycles. Moreover, the CV profile maintained its rectangular shape, suggesting that the electrolessly deposited vanadium oxide is structurally stable. To further examine

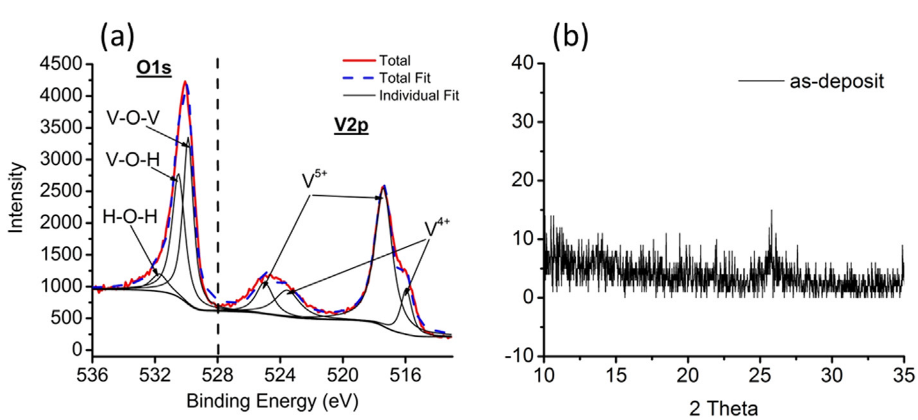

Fig. 3. (a) High resolution XPS spectra for V2p and O1s; (b) XRD pattern of vanadium oxide electrode.

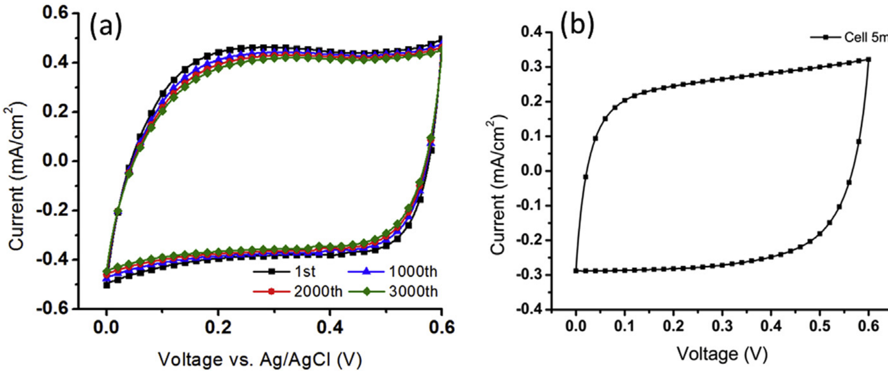

Fig. 4. CVs of (a) vanadium oxide electrode at 1st, 1000th, 2000th and 3000th cycle in 1 M LiCl at 5 mVs^{-1}; (b) an EC cell made from two identical vanadium oxide electrodes in 1 M LiCl at 5 mVs^{-1}.

its suitability for EC applications, a 2-electrode cell was assembled using two 0.5M–5days electrodes separated by a thin filter paper soaked in 1 M LiCl. The CV of this device is shown in Fig. 4(b) and displays a rectangular profile. The cell voltage in Fig. 4(b) is limited to 0.6 V, which could be further improved by leveraging an asymmetric configuration as suggested by Deng et al. [18].

While the electrolessly deposited vanadium oxide is promising as electrode material for EC applications, the mechanism of deposition, the actual compositions, and the microstructure of vanadium oxide need to be further studied, in order to optimize the processing conditions and to improve the performance, conductivity and stability of the deposited vanadium oxide. These are subjects of future investigations.

4. Conclusions

A simple and inexpensive electroless deposition method was leveraged to produce vanadium oxide electrodes for EC applications. An optimized processing condition was identified. Material characterizations revealed a meso- and macro-porous structure on the electrode surface. Surface and structural analyses showed that the composition involved both VO_2 and V_2O_5 and that the mixed vanadium oxide was in the amorphous state. Rectangular CVs and good cycle life of the electrodes suggest that vanadium oxides produced by the described electroless deposition method are promising as high performance EC electrode materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.08.034.

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